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Permeable epoxy coating with reactive solvent for anticorrosion of concrete

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A B S T R A C T

Concrete usually suffers from deterioration caused by ions and water soaking in the cracks, pores and other defects. We have prepared epoxy solution with carbonyl solvent, where the solvent and epoxy can react with amine (curing agent) to form network. The epoxy solution has remarkable wettability on concrete surface, and it can even permeate into the pores or defects in concrete. After coating with the epoxy solution, the strength of the concrete can be improved to above 9.3 MPa. Particularly, the coated concrete exhibits excellent anticorrosion performance with total charge passed in chloride permeability as low as 130 C.

1. Introduction

Concrete has been extensively applied in constructions for over one hundred years. Its solidification usually yields pores or defects in different sizes, which allows water and ions to enter, leading to the corrosion of concrete [1–3]. The corrosion brings serious economic and safety problems since it shortens the service life and reduces the strength of buildings.

Coating is one of the most effective and simple approach to inhibit concrete corrosion [4–6]. Generally, a large amount of solvent is used to reduce viscosity of coating so that the polymer can permeate into the pores and defects of concrete. If the solvent is not reactive, it would move out of the pores during or after curing so that the pores cannot be completely blocked. On other hand, the solvents often volatilize during or after curing, which have a negative impact on the environment [7,8]. To solve the problem about solvents, solvent-free coatings have been developed for anticorrosion of concrete [9–11], but their poor permeability due to high viscosity limits their application [12]. Alternatively, silane with low molecular weight was used to inhibit the penetration of water or water-born ions in concrete. However, it only covers on the capillary pores, and the mechanical properties of concrete is slightly improved [13,14].

Epoxy based coatings have been used to protect the concrete due to their excellent chemical resistance and mechanical properties [15–18]. Also, epoxy itself does not release toxic substances such as BPA after curing [19,20]. In the present work, we have developed an epoxy based coating with reactive solvent containing carbonyl groups. The solvent and epoxy can react with amine and form a network. In particular, the coating has low viscosity and excellent wettability before curing so that it can permeate into the pores in concrete to improve its strength and anticorrosion. We have examined their wettability, permeability and mechanical properties of the coatings. Also, we studied the reaction and permeation mechanism of the coatings. Our aim is to develop high performance epoxy coating for concrete.

2. Experimental section

2.1. Materials

Diglycidyl ether of bisphenol A (DGEBA) with epoxide equivalent weight (EEW) of 180–190 g/equiv was from Nantong Xingchen Synthetic Material Co. Furfural, acetone, methyl isobutyl ketone (MIK), xylene, diethylenetriamine (DETA) and 2,4,6-Tris-(dimethylamino-methyl) phenol (DM*P*-30) were purchased from Guangzhou Chem. Reagent Co. Neopentyl glycol diglycidyl ether (NGDE) was from Xinyuan Chem. Co. Portland cement was from Zhujiang Cement Co. Machine-made sand and aggregate were from Bailitong Building Material Co. All the chemicals were used as received.

2.2. Preparation of epoxy coating

The coating was composed of component A and B, where A consisted of epoxy and solvent and B was the combination of DETA and DM*P*-30 used as the curing agent. The coatings with xylene, acetone, furfural, furfural-acetone mixture, MIK and NGDE as the solvent was designated as Ep-X, Ep-A, Ep-F, Ep-FA, Ep-M and Ep-N, respectively. NGDE with epoxy groups is a well-known reactive solvent for epoxy. The formulation is as follows: 40–45 wt% of epoxy, 40–45 wt% of solvent, 10–15 wt% of DETA and 1–2 wt% of DM*P*-30.

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2.3. Preparation of concrete and mortar

P.II 42.5 Portland cement (Table S1) was used. The mortar specimen was prepared in water/cement/sand ratio of 0.5/1.0/3.0. The concrete specimen was prepared in water/cement/aggregate ratio of 0.5/1.0/6.0 (Table S2). Both the concrete and mortar specimens were cured in wet chamber with relative humidity of 100% at 20 °C for 28 d and subsequently dried at 110 °C for 1d in the oven. The characterization of the pores in the mortar and concrete can be found in Table S3 and Fig. S1.

Prismatic mortar specimen was casted as the substrate for contact angle tests and pull-off strength tests of epoxy solution. The specimen used was 20 mm × 20 mm × 20 mm in the contact angle test and 100 mm × 100 mm × 20 mm in the pull-off test.

Columned concrete specimen (Φ100 mm × 100 mm) was casted and cut into smaller one (Φ100 mm × 50 mm) with both ends eliminated, and it was used as the substrate for chloride permeability tests of epoxy coating.

2.4. Characterization

2.4.1. Fourier transform infrared spectroscopy (FTIR)

FTIR spectra were recorded on VECTOR-22 IR spectrometer (Bruker). The spectrum was collected from 64 scans with a spectral resolution of 4 cm^{-1} by KBr disk method.

2.4.2. Solid content measurements

The solid content of epoxy coating was determined by placing 3 g of solution on a culture dish with diameter of 75 mm according to ISO 3251 [21]. The specimen was cured at 20 °C for 7 d and subsequently dried in an oven at 125 °C for 1 h. The solid content was determined from the change of mass. Five tests for the same epoxy solution were conducted to obtain an average value.

2.4.3. Viscosity measurements

The viscosity of epoxy solution without curing agent was measured on AR-G2 rheometer (TA Instruments) at 25 °C.

2.4.4. Surface tension measurements

The surface tension of epoxy solution without curing agent was measured at 25 °C for 5 min on Sigma 701 Tensionmeter (KSV) by using the Du Nouy ring method.

2.4.5. Pull-off strength tests

Epoxy solution was coated on the mortar specimen with a dosage of 0.6 kg/m^2. The specimen was cured at 25 °C for 14 d. The pull-off strength was measured by using PosiTest AT-A pull-off adhesion tester (DeFelsko) according to ASTM D 7234 [22]. The measurement area is 20 mm in diameter and the pull rate was set at 0.2 MPa/s. Five different points on each sample were tested to obtain an average value.

2.4.6. Contact angle measurements

The sessile drop method was conducted on Theta Auto 113 (KSV) by placing 5 μL epoxy solution without curing agent on the mortar surface. The mortar surface was polished by 250 mesh emery paper. After dispensing, the shape of droplet was monitored with a digital camera. Five different regions of each sample were measured to obtain an average value.

2.4.7. Wettability measurements of porous materials

The wettability of powder or porous materials can be characterized by using the capillary rise method [23–26]. A liquid would rise into the pores of the solid due to capillary action. When a porous solid is bc obtained by Washburn equation [27].

$$t = \left(\frac{\eta}{C\rho^2\gamma\ \cos\ \theta}\right)w^2 \quad (1)$$

Here, t is the exposure time of liquid for mortar, w is the weight of epoxy solution permeating into mortar, η is the viscosity of epoxy solution, C is material constant related to the size of pores in mortar, ρ is the density of epoxy solution, γ is the surface tension of epoxy solution and θ is the contact angle between mortar and epoxy solution. Ep-A was used as the reference. Capillary rise weight (w^2) in the mortar as a function of time of epoxy solution before curing was measured by using Sigma 701 Tensionmeter (KSV). For each solution, five specimens were measured to obtain an average value.

2.4.8. Chloride ion permeability tests

Epoxy solution was coated on one face of columned concrete specimen with the same dosage and curing time in the adhesion tests [28–30]. After curing, the specimen was saturated with water under vacuum, and paraffin was applied to the curved surfaces of the discs in case water and ions leak from the specimen. The chloride permeability was measured by using NEL-PER concrete permeability tester (Naier Instruments) according to ASTM C 1202 [31]. Each coating was measured with three specimens to obtain an average value.

3. Results and discussion

We first examined the reaction of solvent containing carbonyl groups. Fig. 1 shows FTIR spectra of the coatings with a typical carbonyl solvent (MIK) and a non-carbonyl solvent (xylene). For Ep-X, the bands do not change with time before and after curing, indicating xylene is inert or non-reactive. In contrast, we can observe a new band at 1648 cm^{-1} assigned to the C═N stretching vibrations in Ep-M after 12 h, indicating that carbonyl solvent and amine react yielding Schiff base [32,33]. Namely, MIK can not only act as a diluent of epoxy but also react with amine to chemically link with epoxy. Actually, we also examined other carbonyl solvents including acetone, furfural and furfural-acetone mixture, they can chemically link with epoxy via amine (Fig. S2). Like NGDE, they are reactive solvents.

Fig. 2 shows the solid content of epoxy coatings with different solvents after curing, where the solid content reflects the degree of reaction of the system. For Ep-X, the solid content (56.8 wt%) is close to the theoretical value (56.5 wt%). This is understandable because xylene does not react with other components. In contrast, Ep-N shows the highest solid content (98.5 wt%) because the solvent completely reacts with the amine. For Ep-A, Ep-F, Ep-FA and Ep-M with carbonyl solvents, the solid contents are 64.2 wt%, 79.1 wt%, 85.6 wt% and 67.0 wt %, respectively. Note that some solvents volatilize during curing

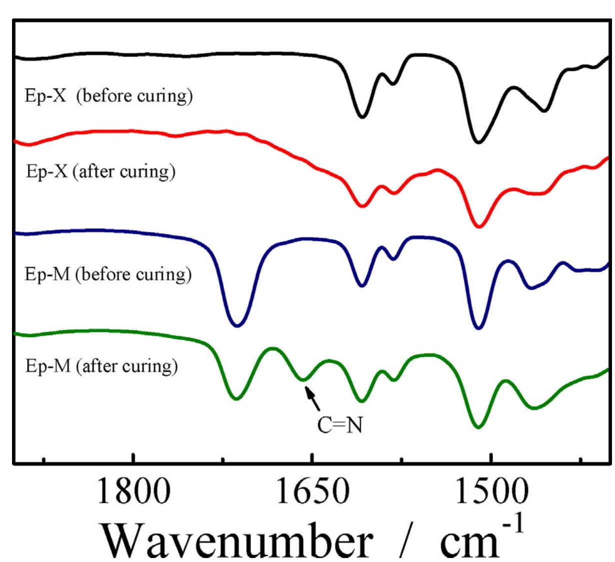

Fig. 1. FTIR spectra of epoxy coatings before and after curing of 12 h.